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Microbial bioelectrochemical reactor for wastewater treatment applications

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Abstract

A microbial BioElectrochemical Reactor (BER) was employed for the degradation of an azo dye. Electrodes inside the BER were made of stainless steel mesh and were packed with activated carbon. Dye degradation and aromatic reduction products (e.g. aromatic amines) were analyzed. Dye removal was from 99 to 90% upon changing the residence time from 4 to 1 h in single pass mode; degradation of aromatic compounds was higher with increasing time. Electrical stimulation of the bioreactions decreases the reactor residence time at higher removal rates in comparison to a simple biotic system.

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Keywords: bioelectroreactor, azo dye degradation, current stimulated biodegradation, activated carbon, hydrodynamic analysis

1. Introduction

Microbial bioelectrochemical systems are applied to wastewater treatment processes in two ways: it can be used to produce energy (Microbial Fuel cell), to improve the degradation of specific organic pollutants and/or produce biofuels (Microbial Electrolysis Cell; MEC). Bioreactors configured as MEC (MBER) have increased interest due to the many benefits that can be obtained, such as higher degradation efficiency, specific metabolites or biofuels synthesis.

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In general, studies about the degradation of specific pollutants in water using MBER like Phenol[1], Endocrine disruptive estrogens[2], and Trichloroethene[3], etc., comprise typical batch configurations on one or two chamber cell and are focused on the enhancement and understanding of kinetic effects and electron transfer mechanisms; the operational conditions of this systems makes difficult to analyze the effect of transport phenomena and determine scaling parameters. Continuous systems, in contrast to batch cells, offer the possibility of operating with lower residence time and treat larger water volumes.

Continuous flow MBER systems have been studied generally for wastewater denitrification[4,5,6] due to the proved increased efficiency in reduction reactions. These studies highlighted in their conclusions the importance of controlling the process pH and the hydraulic residence time (HRT) of the reactor. More recently, MBER has been proved for the treatment of complex organic pollutant degradation in water, as azo dyes, chlorinated organic and simultaneous biofuel generation, either methane or hydrogen[7,8] focusing on the effect of cathode potential on degradation efficiency.

In a previous work, a batch MEC, as single chamber, was developed to study the degradation of a textile azo dye[9]. In this system, it was analyzed the influence of activated carbon on the cell and the intensity of the applied direct current on the kinetic of dye biodegradation and microorganism viability. The results showed that by applying 1 mA at MEC, dye removal increased by 26.1% against the biotic control, and there was an effect on microorganism's growth increasing by 40% of biomass as VSS; in addition, it was observed that activated carbon allowed buffering of Open Circuit Potential and pH in the solution. These results lead to set up a continuous process, an Upflow Fixed bed bioelectroreactor. This kind of reactor is suitable in order to direct the flux of the solution in the order that benefit the reactions of interest; in this case for azo dye degradation the reaction is oriented as reduction – oxidation. A conceptual scheme of the process is shown in Fig. 1.

This work presents the development of a bioelectrochemical system for degrading a reactive azo dye (reactive red 272); this dye was chosen as it is persistent in wastewater discharges of textile industries and has biological hazardous characteristics. Therefore, a cylindrical upflow fixed bed bioelectrochemical reactor (UFB-BER) was developed using granular activated carbon (GAC) as support media. It was studied how electrochemical and hydrodynamic parameters affect the efficiency and kinetics of the system.

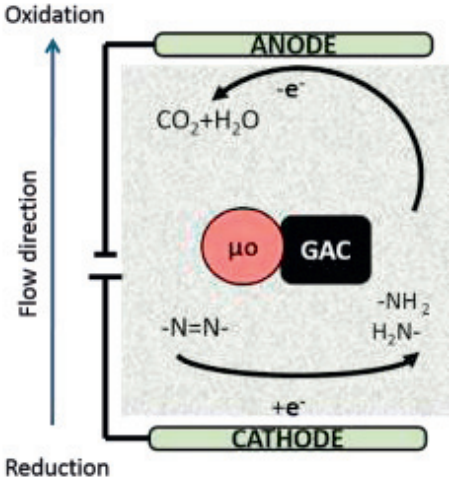

Fig. 1. Schematic diagram of the microbial bioelectrochemical reactor configuration.

2. Materials and methods

2.1. Microorganisms source and preparation

A microorganism's consortium was obtained from cow ruminal content and was adapted for azo dye biodegradation. To achieve this, a solution containing 500 mgL-1 of Reactive Red 272 dye (RR272), yeast extract

and dextrose 10% v/v was prepared; this solution was changed every week for a fresh one. In order to take the microorganisms growth to the exponential phase, a basal media was prepared: NH_4Cl 3 g, K_2HPO_4 1 g, $MgSO_4 \cdot 7H_2O$ 0.25 g, KCl 0.25 g, $FeSO_4 \cdot 7H_2O$ 0.002 g and yeast extract 0.3 g, all dissolved in 1 L distilled water, adjusting the solution pH to 7.0 – 7.4; 5 mL of the microbial consortium were added to 200 mL of the basal media and were incubated for 72 h. This process was carried out two times continuously using the previous solution to inoculate fresh basal media but adding 100 mgL-1 of RR272. This media was used to inoculate the bioreactor.

2.2. Batch study for kinetic analysis

A parallel plate´s cell batch BER, 200 L volume pyrex glass, was set towards the study of the effect of applying an electric field on microorganisms; the electrodes were flat plate stainless steel 316L separated by 2.2 cm, and a surface area of 25.35 cm^2. Constant current flow was applied by the power source. Dye degradation was analyzed applying 1 mA (0.039 mA/cm^2) at a solution of 100 mgL^{-1} of RR272 and inoculated with microorganism of the consortium described previously. No other carbon source was used. The increase in VSS (Volatile Suspended Solids) was measured at the end of each test and de degradation activity for the azo dye was calculated.

2.3. Microbial bioelectrochemical reactor set-up

A cylindrical Upflow Fixed Bed BER (UFB-BER) was constructed with acrylic, with a total volume of 523 cm^3 and packed with 142 cm^3 GAC as shown in Fig 2; GAC was previously saturated with RR272 dye and inoculated with the microorganisms consortium described in section 2.1. Electrodes were circular (6 cm diameter) from 304L stainless steel mesh (wire = 0.37 mm) and ageometric surface area of 111.8 cm^2. The cathode was located in the lower part of the cell and the anode 6 cm separated above from the former, in order to force the flux to pass through the electrodes from cathode to anode. The reactor was operated in a continuous recycling mode and in a single stage at a half residence time (RTh) of 1 and 4 h; RR272 dye concentrations employed were100, 200 and 500 mgL^{-1}. The characteristics of the UFB-BER are described in Table 1.

Table 1. UFB-BER Characteristics

Entry	Value
Reactor volume, L	0.649
Fixed bed volume, L	0.427
Internal diameter, cm	6.350
Fixed bed length, cm	13.50
Total length, cm	20.50
Bed porosity	0.035
Electrodes surface area, cm^2	111.83
Electrodes separation, cm	6

2.4. Analytical methods

Dye concentration was analyzed by UV/Vis spectrometry at 505.6 nm (GBC spectrophotometer model CINTRA 101). The concentration of microorganisms was determined as Volatile Suspended Solids (VSS); Chemical Oxygen Demand (COD) was measured using the closed reflux Colorimetric Method, according to Standard Methods[10].

3. Results and discussion

3.1. Batch Kinetic analysis

The biodegradation of the dye was analyzed in the 200 mL parallel plates BER in three modes: 1) applying 1 mA of direct current resulting in a density of J=0.039 mA/cm2 (5 mA/L dye solution) and inoculated, 2) without applying electric field, 3) applying the same intensity of electric field but without microorganisms; all systems without a carbon source or GAC. The results showed that with the application of the electric field, the removal (reduction) of the dye is 98%, and without is 71.9% in the same reaction time (Fig. 2). The system without microorganisms did no remove any color from the solution and so, initial concentration was kept constant discarding a direct electrochemical reduction of the dye by the electrodes.

Degradation activity and reduction rate of the dye was higher in the BER under the effect of the electric field and showed a marked dependence with dye concentration, decreasing as color was consumed. On the contrary, the biotic degradation activity of microorganisms showed a slight variation with the concentration at the beginning and afterwards was kept constant, which explains a different reaction mechanism.

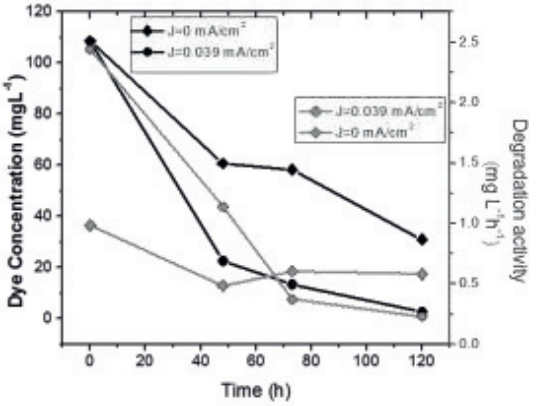

Fig. 2. Dye degradation kinetics and activity, with and without the application of an electric field (J=0.039 mA/cm^2).

3.2. Reactor Evaluation

Dye biodegradation on the bioreactor was analyzed before applying electrical current, in recycling mode. Fig 3A shows the reduction in the absorbance of the RR272 dye solution at 500 mgL^{-1} in the adaptation period with GAC (adsorption period) with a removal rate of 88%, and after inoculation with the microbial consortium (adaptation period), in which case dye reduction was 100% at 73 h. After this adaptation period, electrical stimulation was applied. Fig 3B shows the difference in dye removal with the application of a J=0.045 mA/cm^2 to the reactor and a RTh of 4 h. Azo dye RR272 was degraded in water solution by the UFB-BER without the need of a main substrate as glucose.

Afterwards, as a microbial bioelectrochemical system, the UFB-BER efficiency was studied working on average residence times (RTh) of 1 and 4 h, initial dye concentration of 100 and 200 ppm, and applying 5 mA of direct current resulting in a density of J=0.045 mA/cm^2. Results showed that dye removal at 1 h of RTh was significantly improved by applying electrical stimulation, increasing from 70% (without applying current) to 98%, leading to degradation ratios similar to those obtained at 4 h of RTh, in a single pass mode (Fig. 4) that the difference between applying an electric current to the bioreactor is not significant at RTh of 4 h, but it is considerable at RTh of 1 h; therefore, when applying electrical stimulation, the resulting removal rate is similar at 1 and 4 h of RTh. This explains that the contribution of applying an electrical stimulation consist in the decrease of reactor residence time at higher removal rates, in comparison to a simple biotic system in a continuous flow mode. This decrease is important because it allows to increase the volume of wastewater treated or to reduce the volume of a process in a real scenario.

In order to analyze the degradation efficiency at a higher concentration, an experiment was carried out using a 500 ppm of RR272 solution, J = 0.045 mA/cm^2 and 4 h of RTh in the UFB-BER operating in recycle mode; UV/Vis spectra of the effluent were obtained after each stage (Fig 4B). A dye removal rate of 96.5% was achieved in one step but, as it is shown in Fig. 6A, it was necessary 3 reaction steps to decrease the intensity of the signals in the UV region (200-400 nm), related to degradation of aromatic compounds produced as dye reduction byproducts. This result shows a synergic effect between both microorganism's metabolisms an electrical stimulation, allowing higher degradation rates of the RR272 dye molecule, reducing also the concentration of aromatic compounds in the effluent that could cause toxicity (e.g. aromatic amines).

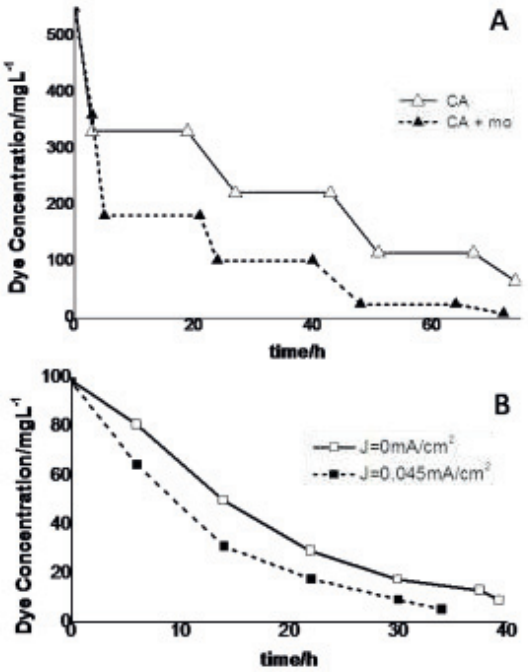

Fig. 3. **A**. Dye reduction in the UFB-BER inoculation stage at 500 mgL^{-1}, and comparing the saturation with CA (Δ) and the biological removal (▲), operating in recycling mode. **B**. Dye reduction in the UFB-BER comparing the effect of applying (□) and not applying (□) electric stimulation at J=0.045 mAcm^{-2} and inlet dye concentration of 100 mgL^{-1}, operating in recycling mode (RTh 4h).

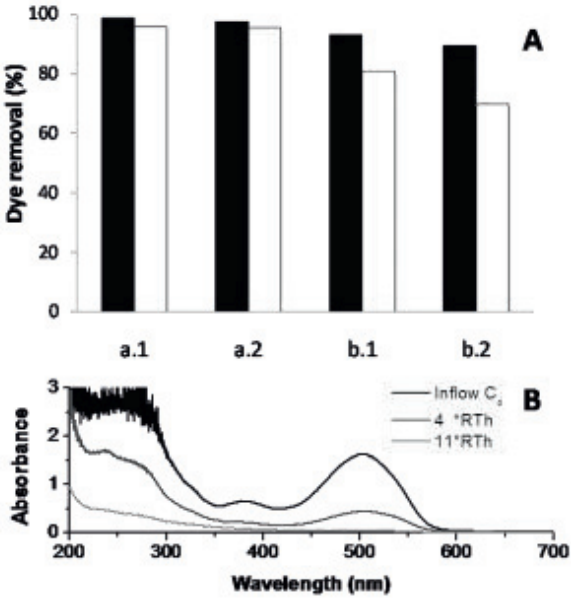

Fig. 4. **A**. Dye degradation % in the UFB-BER.■: J=0.045 mA cm^{-2}; □: J=0 mA cm^{-2}. a: RTh 4h, b: RTh 1h, 1: 200 mgL^{-1}, 2: 100 mgL^{-1}. **B**. UV/Vis spectra of UFB-BER effluent in recirculation mode, RTh= 4h, J=0.045 mA $cm^{-2}$and initial dye concentration= 110 mgL^{-1}. * RTh means the number of residence times that the solution has been recirculated.[9]

4. Conclusion

The application of an electric current to a microbial reaction system increases the azo dye degradation rate without the need of an extra carbon source or electron donor, due to the stimulation of the extracellular reactions and the stress induced on the microorganisms. A synergic effect of the electrical and biological parameters allowed reducing the residence time of the bioelectrochemical reactor without affecting the degradation efficiency in a continuous flow process.

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